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PART III: Environmental Fate

Chapter 4

PULSED BIOSPARGING OF A RESIDUAL FUEL SOURCE EMPLACED AT CFB BORDEN

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ABSTRACT

Biosparging enhances both aerobic biodegradation and volatilization and is commonly applied to residual hydrocarbon source zone remediation. This technology was applied in pulsed mode to a known source of gasoline contamination in order to quantify the extent of remediation achieved in terms of both mass removed and reduction in mass discharge into groundwater. The gasoline source was created at the groundwater research facility at CFB Borden, Canada. About 40 L of gasoline with 10% ethanol was injected in small volumes from 24 injection points below the water table in 2004. The downgradient plume is still being monitored and the source area was cored in 2007. In 2008, a single-point biosparge system was installed and operated. Water-saturated soils precluded the use of a traditional soil vapor extraction (SVE) system, so an airtight cover was used with soil venting to capture and monitor off-gases. Conservative tracers (He, SF₆) and hydrocarbon gas monitoring were intended to assign mass removal to volatilization. CO₂ and O₂ monitoring in the off-gas confirmed limited biodegradation of hydrocarbons. Post-remediation core analysis and downgradient monitoring of groundwater will be used to define the extent of remediation and decline of mass discharge to the groundwater plume.

Keywords: pulsed biosparging, air sparging, soil vapor extraction, gasoline, remediation

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1. INTRODUCTION

Gasoline is a near-ubiquitous subsurface pollutant in North America and a number of technologies are available for remediation. This paper describes some preliminary findings from an investigation of pulsed air sparging applied to treat a small gasoline residual source emplaced in a shallow sand aquifer at CFB Borden, Canada.

In situ air sparging (IAS) was first used as a treatment technology in the mid-1980s (Bass et al., 2000). Volatilization and O₂-enhanced biodegradation are the mass removal mechanisms. Soil vapor extraction (SVE) is normally used to collect the air sparging gas as it migrates through the vadose zone to ground surface.

IAS has been used to clean up contaminated sites for several years and the general mechanisms for treatment of gasoline sources are relatively well understood. When used appropriately, air sparging has been found to be effective in reducing concentrations of volatile organic compounds (VOCs) found in petroleum products. Pulsed air sparging, in which the air sparging is turned on and off (generally based on aquifer response), has been found to be more effective than continuous air sparging in several theoretical (Johnson, 1998 and Ahlfeld et al., 1994) and field studies (Kirtland et al., 2001; and Yang et al., 2005).

The total hydrocarbon mass removed by an IAS/SVE system is difficult to predict and quantify because of the heterogeneous nature of the soil gas flow paths (Johnson, 1998). In this study, one of the main objectives was to quantify the mass removed through volatilization and biodegradation from a relatively well-known source zone using pulsed IAS, and to determine the effect of this treatment on downgradient dissolved BTEX concentrations.

2. MATERIALS AND PROCEDURE

2.1 Site Description

The field site is located at Canadian Forces Base (CFB) Borden, 100 km north of Toronto, Ontario, Canada.

The Borden water table aquifer is in a relatively homogeneous, clean, well sorted fine to medium sand extending 7 to 8 m below ground surface (bgs). The hydrogeological properties of the Borden sand aquifer have been studied extensively (Mackay et al., 1986, and Sudicky et al., 1983;). The Borden sand aquifer is generally homogenous; the hydraulic conductivity of core sections taken from within the source zone ranged from 4.3×10^{-5} to 1.5×10^{-4} m/s (Yang, 2008). Yang also observed a relatively lower hydraulic conductivity zone ranging from 3.2 to 3.6 m bgs and relatively higher hydraulic conductivity zones at about 2.5 and 4.5 m.

About 40 L of American Petroleum Institute (API) gasoline containing 10% ethanol was emplaced below the water table between October 8 and 13, 2004 (Mocanu, 2007). The pulsed sparging experiment was conducted on this emplaced source zone, which is denoted as the E10

residual source. The E10 residual source is bounded by two rows of sealable sheet piling driven to a depth of 7 m. The resulting dissolved phase plume was monitored extensively using a network of four rows of multilevel monitoring wells, three of which were located downgradient of the E10 residual source. Each row contained seven wells with 15 monitoring points each.

Sparging in the area of E10 residual source began on April 28, 2008. At this time the solubility analog of Raoult's Law (King and Barker, 1999) was used to estimate that all the ethanol had been leached from the source and that about 22 kg or 30 L of gasoline residual remained. Soil cores collected in 2007 (Yang, 2008) suggested that the residual gasoline had not spread significantly away from injection wells used for source emplacement and that NAPL was still present in the source zone as expected (Figure 1).

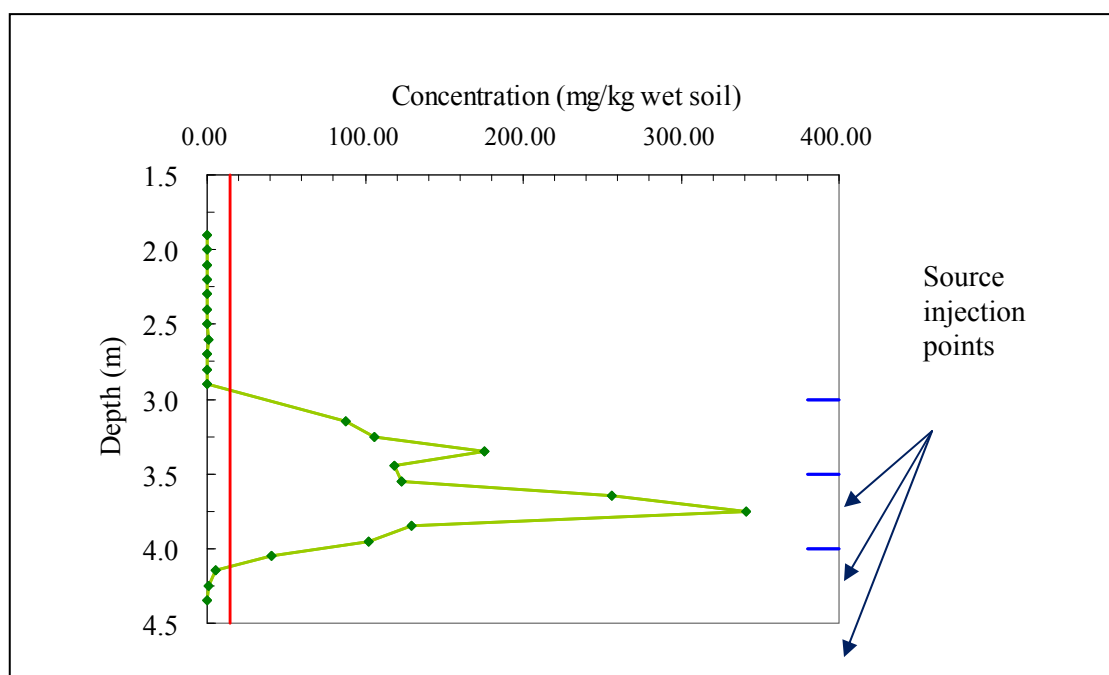


Figure 1. Profile of total analyzed hydrocarbon concentrations (BTEX, trimethylbenzene, and naphthalene) from the center of the E10 residual source zone. The vertical line (16.66 mg/kg wet soil) indicates the concentration above which free product is assumed to be present (Yang, 2008).

2.2 Treatment System

The air sparging system consisted of 3 injection points arranged in a line across the source zone. The injection points were driven using a jackhammer to minimize soil disturbance around each point. Each sparge point was 20 cm long and 3 cm in diameter, with four 8-mm holes covered with stainless steel mesh located every 2.5 cm along the length of the housing. The sparge point was connected to the compressor by 1 cm ID teflon tubing. The top of the screen

was set at 5 m bgs; 1 m below the residual zone (3 to 4 m bgs). Air was injected at a flow rate of 35 L/min. A pulsed-sparging system was used with an on/off cycle based on aquifer pressure response times.

In April the water table at this location rose above ground surface. The aquifer material (clean sand) and extent of water above ground surface ruled out dewatering the area to a sufficient depth to allow the use of a standard SVE system. Instead, a 7 m x 7 m box was constructed to contain soil vapor escaping from the soil surface. Two air pumps were connected in series to an outlet at the top of the box. During sparging, the flow rates were adjusted so that the flow rate out of the box was slightly higher than the flow rate into the subsurface (approximately 100 L/min). This minimized leaks of sparged gas outside the box.

The treatment system included ports for injecting SF₆ and helium for tracer tests, sample ports for injected and removed air, and two pairs of piezometers inside and outside the box. Transducers were placed in each piezometer to record water pressure changes during treatment (Figure 2). The system was operated from April 28 to June 23, 2008. The off-gas collection system ran for approximately 280 hours over the 33 days of active sparging. It was operated for a half hour prior to initiating a sparging episode and for at least 2 hours at the end of a sparging episode. The total length of time that the air injection system operated was 98 hours, less than half the total time to off-gas extraction system operated.



Figure 2. Treatment system setup with dashed oval around piezometers inside the box, white circles around air sparging points, and black circle around vapor extraction point. Monitoring row 2 is in the foreground. It is covered by the treatment system in the cell used for this experiment.

2.3 Groundwater Sampling

Groundwater samples were collected before and after treatment from the multilevel wells located downgradient of the gasoline source. The post-treatment sampling was conducted at the end of July 2008, when the groundwater from the last day of treatment should have reached this location based on an estimated advective travel time. This was assumed to be the best time to capture remediated groundwater leaving the source prior to potential concentration rebound.

2.4 Sample Analysis

Off-gas was continuously monitored for VOCs using a mini-RAE 2000 photo-ionization detector (PID). Off-gas air samples were also collected at regular intervals for hydrocarbon analysis using a Hewlett Packard 5890 gas chromatograph (GC). Groundwater hydrocarbon samples were analyzed using the same equipment. Off-gas samples were also analyzed for O₂ and CO₂ using a Fisher/Hamilton Model 29 gas partitioner or a GOW-MAC (series 350 GP) GC. The latter equipment was only used to determine CO₂.

Helium tracer tests were conducted throughout the treatment period to determine how much of the injected air was recaptured in the off-gas collection system. Helium was analyzed in the field using a Dielectric MGD-2002 helium detector. SF₆ was injected during the last day of sparging to determine how much of the injected O₂ had dissolved into the groundwater and was captured in the off-gas and groundwater samples. SF₆ concentrations were determined using a Shimadzu GC-9A gas chromatograph equipped with an electron capture detector. These tracer data were inconclusive because of helium loss prior to injection. However, visual evidence (lack of bubbles on the standing water) does not indicate significant loss of sparged gas. For simplicity, at this stage of analysis, we have assumed that all sparged hydrocarbons are considered to have been collected by the gas extraction system.

3. DATA AND ANALYSIS

3.1 Water Pressure fluctuations

Pressure transducer data indicated that the water pressure maximized within about 5 minutes of starting the air sparging system and then quickly dropped off (Figure 3). Based on this response the pulse sparge cycle time was set at 1.25 hour based on this response.

The strongest pressure responses were observed in the deeper transducers (closer to the sparging point screen) and in the ones within the air collection box. The transducer data inside the box indicated an above-ground piezometric surface, which was consistent with visual observations of groundwater mounding just outside of the gas extraction box.

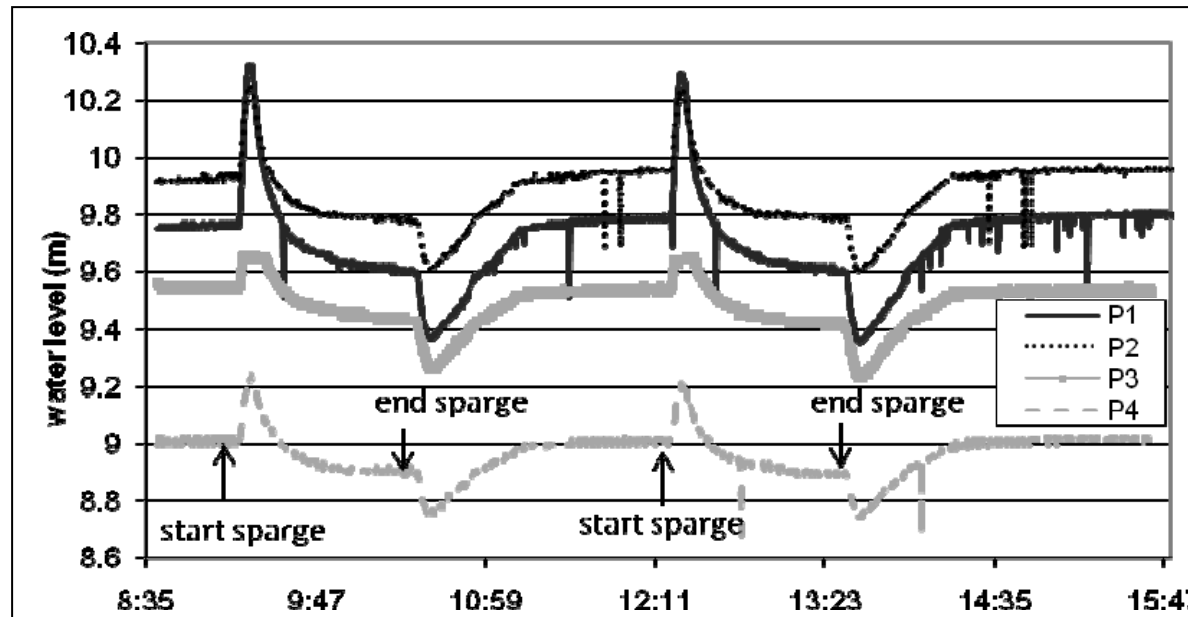


Figure 3. April 30 transducer data showing aquifer response to pulsed sparging. P1 and P2 are inside the box; and P3 and P4 are outside. P1 and P3 are deeper. The ground surface elevation was set at 10 m.

3.2 Off-Gas Data

The hydrocarbon gas concentrations peaked in the first 16 hours of system operation, when the central sparging point was used, and then declined thereafter (Figure 4). The second concentration peak at approximately 100 hours corresponds to a switch to the second air injection point. The third injection point was used only briefly due to equipment issues at 140 hours and then again from 230-240 hours.

The PID data do not show any short duration peaks that would have been missed by the sampling schedule adopted. They confirm the representativeness of the samples collected for GC analysis. The PID gives a total VOC concentration and is used to define trends in individual compounds and the F1 hydrocarbon fraction with actual values taken from the GC analyses.

Off-gas concentrations declined sufficiently for the system to be turned off after 270 hours of active sparging. Sparging of the most volatile constituents (pentane and hexane, 526 and 150 mm Hg) far exceeded sparging removal of the target monoaromatics (average 13 mm Hg). Vapor pressures are from Montgomery, 2000. Approximately 80% and 50% of the pentane and hexane present in the residual gasoline were recovered in the gas collection system. Only about 4% of the TEX was recovered (benzene was detected in the off-gas).

CO₂ concentrations increased and O₂ concentrations decreased slightly from baseline concentrations (Lambert, 2008). This confirms that some aerobic biodegradation was occurring.

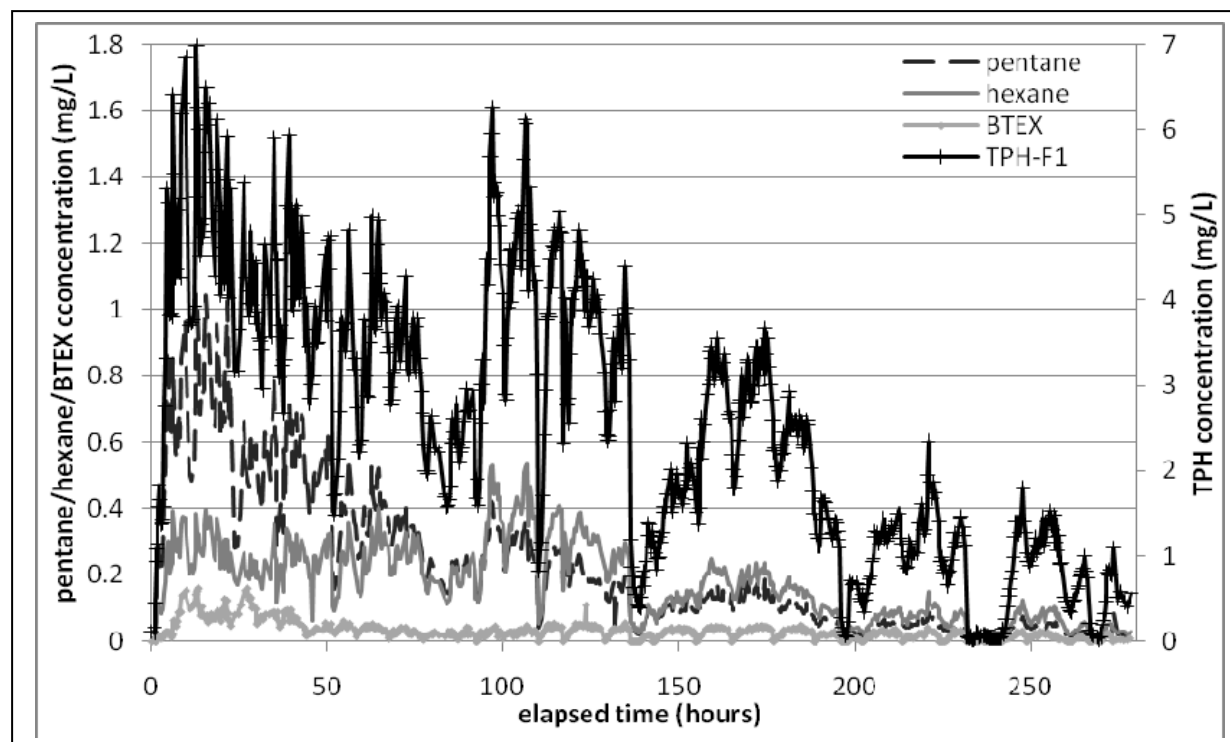


Figure 4. GC concentrations over the course of sparging. Note that the elapsed time represents the time of active soil gas extraction system operation and not the duration of the investigation.

3.3 Groundwater Data

Post-sparging groundwater results collected in 2008 indicate a 27% decrease in the benzene mass flux, a 92% decrease in the toluene mass flux, a 65% decrease in the ethylbenzene mass flux, a 6% decrease in the p/m-xylene mass flux, and a 5% decrease in the o-xylene mass flux. However, the hydrocarbon mass flux changes in groundwater before and after treatment did not vary significantly enough from long-term decreases from attenuation to determine the effect of sparging. Groundwater sampling will be repeated in 2009 to determine if the source zone biodegradation has produced a long-term decrease in mass flux.

4. CONCLUSIONS

This study used IAS and an off-gas collection system to remediate a gasoline source where a conventional SVE system could not be installed. During two months of pulsed air sparging, the most volatile hydrocarbons were removed first. Most of the mass removed contained non-BTEX hydrocarbons. CO_2 and O_2 concentrations in the off gas indicate that oxygen added to the subsurface was used for microbial activity. Only a small percentage of the BTEX mass estimated in the source zone was captured by the SVE system, and this system did not have a clear effect

on downgradient groundwater BTEX concentrations. Additional groundwater sampling continues to determine the long-term impact of the sparging system on plume behavior.

This study suggests that a significant amount of hydrocarbon mass may need to be removed before air sparging has an impact on downgradient concentrations. The variability of hydrocarbon removal rates in the off-gas also demonstrates the difficulty of source removal even in a simple aquifer with a small, well-defined source.

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